

# Synthesis and Crystal Structure of a New Paramagnetic Complex Salt of Diprotonated Dioxocyclam with $\text{PtCl}_4^{2-}$ and Water (1:1:1)

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**Abstract.** The paramagnetic complex salt of diprotonated dioxocyclam (1,11-dihydro-5,7-dioxo-1,4,8,11-tetra-azacyclotetradecane), Pt(II) tetrachloride and water has been synthesized in strongly acidic medium and identified by X-ray structure analysis. The crystals of  $[(\text{C}_{10}\text{H}_{22}\text{N}_4\text{O}_2)^{2+}(\text{PtCl}_4)^{2-}]\cdot\text{H}_2\text{O}$  are monoclinic, space group  $P2_1c$ ,  $M_r = 585.23$ ,  $a = 9.516(1) \text{ \AA}$ ,  $b = 11.926(1) \text{ \AA}$ ,  $c = 16.622(2) \text{ \AA}$ ,  $\beta = 102.88(2)^\circ$ ,  $V = 1839(1) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 2.114 \text{ g cm}^{-3}$ ,  $\lambda(\text{MoK}\alpha) = 0.70930 \text{ \AA}$ ,  $\mu = 83.1 \text{ cm}^{-1}$ ,  $F(000) = 1128$ ,  $T = 292 \text{ K}$ ,  $R = 0.019$  for 2808 observed reflections with  $I > 3\sigma(I)$ . Alternating moieties of diprotonated dioxocyclam and a  $\text{PtCl}_4^{2-}$  anion form columns running down the  $c$  axis. Water molecules are localized in the intercolumnar space and contribute to the extensive hydrogen bond network. The macrocycle conformation is characterized by two sequences of torsional angles, corresponding to two different subunits. The shorter sequence idealized as  $(-sc, ap, -ac, +ac, ap, +sc)$  [ $sc(\pm 60^\circ)$ ,  $ac(\pm 120^\circ)$ ,  $ap(180^\circ)$ ], describing the  $C_s$  pseudosymmetric part of the molecule, is centered on a  $=\text{CH}_2$  group between the two peptide  $\text{O}=\text{C}-\text{N}-\text{H}$  fragments. The opposite  $C_2$  pseudosymmetric subunit has a nearly  $(-sc, ac, -sc, ap)_2$  conformation. Pt is square planar coordinated by four Cl atoms,  $\text{Pt}-\text{Cl}_{\text{ave}} = 2.306(8) \text{ \AA}$ . The shortest  $\text{Pt}\cdots\text{Pt}$  distance is  $7.200(1) \text{ \AA}$ .

**Key words.** Dioxocyclam, 5,7-dioxo-1,4,8,11-tetra-azacyclotetradecane, platinum tetrachloride, crystal structure, paramagnetic properties of ionic stacked structure.

**Supplementary Data** relating to this article are deposited with the British Library as supplementary publication No. S2134 (13 pages).

## 1. Introduction

The polyamine ligand 5,7-dioxo-1,4,8,11-tetra-azacyclotetradecane (dioxocyclam, L) exhibits coordination properties of both tetraaza macrocycles and dipeptides and has proved to be an excellent complexation agent towards a variety of metal ions [1]. Kimura *et al.* [2, 3] revealed its ability to serve as a selective chelating and extracting agent for Pt(II), and found that different types of Pt(II)-in and -out complexes are formed, depending on the reaction conditions and the presence of reducing agents.

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The amide type of macrocyclic ligands, dioxocyclam in particular, is known to stabilize high oxidation states of a variety of metals, e.g. Cu(III), Ni(III), Cr(V) [1, 4, 5]. Recently, we have demonstrated the formation of transient Pt(III) species as a result of  $\text{PtCl}_4^{2-}$  interaction with different ligands in a weakly basic medium [6] and we have also succeeded in obtaining a paramagnetic Pt(II)–amide complex by the interaction of  $\text{PtCl}_4^{2-}$  and the cyclic amide creatinine in strongly acidic medium, using X-ray diffraction to determine its structure [7].

Considering the ambient coordination properties of dioxocyclam and the marked influence of the reaction conditions on its reaction with  $\text{PtCl}_4^{2-}$  we aimed to obtain either paramagnetic Pt(II)– or Pt(III)–dioxocyclam complexes using the  $\text{PtCl}_4^{2-}$ –dioxocyclam interaction in acidic ( $\text{pH} < 3$ ) as well as in basic ( $\text{pH} \sim 9$ ) media. The present paper reports the X-ray structure and magnetic properties of the complex obtained in acidic medium. The data concerning Pt(III) generation will be published elsewhere.

## 2. Experimental

### 2.1. SYNTHESIS AND ANALYTICAL PROCEDURES

Dioxocyclam was synthesized as described in the literature [8, 9]. The complex salt was prepared by mixing aqueous solutions of  $(\text{NH}_4)_2\text{PtCl}_4$  (Fluka) (0.0935 g) and dioxocyclam (0.0510 g) and adding conc.  $\text{HClO}_4$  or  $\text{HNO}_3$  in order to adjust the acidity up to  $\text{pH} < 3$ . As a result red crystals of  $[(\text{H}_2\text{L}^{2+})(\text{PtCl}_4^{2-})]\cdot\text{H}_2\text{O}$  were obtained.

### 2.2. X-RAY SINGLE CRYSTAL STRUCTURE DETERMINATION

A prismatic-shaped crystal with approximate dimensions  $0.2 \times 0.16 \times 0.16$  mm was glued to the top of a glass capillary and investigated on an Enraf-Nonius CAD-4 diffractometer (graphite monochromator,  $\text{MoK}_\alpha$  radiation);  $\omega/2\theta$  scan: speed 1 to  $7^\circ \text{min}^{-1}$ , width =  $[0.7 + 0.4 \tan(\theta)]^\circ$ . Cell constants were evaluated by refinement of 22 well-centered reflections with  $20.0 < \theta < 21.0^\circ$ . 7689 Reflections were measured in the range of  $(\sin \theta)/\lambda < 0.616$  ( $h = 0$  to 11,  $k = -14$  to 14,  $l = -20$  to 19). Monitoring of three standard reflections every 2 h with intensity variation within 0.7% confirmed the crystal and instrumental stability. Lorentz and polarization corrections and the consequent empirical absorption correction based on  $\psi$ -scans of five suitable reflections (transmission from 81.457 to 99.906%) were applied. The symmetry equivalent reflections were averaged and 3620 unique reflections with  $R_{\text{int}} = 0.022$  remained. The reflection conditions  $h0l$ ,  $l = 2n$  and  $0k0$ ,  $k = 2n$  suggested the space group  $P2_1/c$ . An approximate position of the Pt atom was elucidated from a Patterson map and used in the initial phasing. After the four chlorine atoms were revealed from the difference Fourier map, the  $\text{PtCl}_4^{2-}$  group refinement by full-matrix least-squares on  $F$  lead to  $R = 0.147$ . The subsequent application of difference Fourier and refinement procedures resulted in the final structural model. Final  $R = 0.019$ ,  $wR = 0.023$ , and  $S = 0.730$ ; weight  $w$  was defined as  $4F_0^2/[\sigma(F_0)^2]^2$ . H-atom positions were calculated (macroligand) or localized (water) and refined with fixed  $U = 0.05 \text{ \AA}^{-2}$ . Max.  $(\Delta/\sigma) = 0.073$ , max. resid-

ual density  $0.38 \text{ e \AA}^{-3}$ . No correction for secondary extinction was performed. Atomic scattering factors and anomalous-dispersion coefficients were taken as quoted in the SDP/PDP V3.0 software [10] which was used throughout the calculations, which were carried out on a PDP11/44 computer.

The EPR spectra were recorded on an Bruker B-ER 420 X-band spectrometer.

### 3. Results and Discussion

Final fractional coordinates are listed in Table I. Selected interatomic distances and angles and torsional angles characterizing the macrocycle conformation are given in Table II. The hydrogen bond geometry parameters are summarized in Table III. The macrocycle conformation with the atom numbering scheme is depicted in Figure 1.

Table I. Positional and equivalent/isotropic thermal parameters with e.s.d.s in parentheses.

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}(\text{\AA}^2)$
Pt	0.15279(2)	0.20274(1)	0.15542(1)	0.02529(3)
Cl(1)	0.3709(1)	0.22840(9)	0.12041(7)	0.0378(3)
Cl(2)	0.1465(1)	0.39222(9)	0.18289(6)	0.0380(3)
Cl(3)	-0.0600(1)	0.17302(9)	0.19796(7)	0.0408(3)
Cl(4)	0.1586(1)	0.01671(9)	0.11939(7)	0.0409(3)
N(1)	0.1457(3)	0.4061(3)	0.3774(2)	0.0327(9)
C(2)	0.2859(5)	0.4559(3)	0.4246(3)	0.037(1)
C(3)	0.3897(5)	0.4775(4)	0.3690(3)	0.040(1)
N(4)	0.4390(3)	0.3763(3)	0.3349(2)	0.0358(9)
C(5)	0.5443(4)	0.3119(3)	0.3788(2)	0.033(1)
C(6)	0.5875(5)	0.2109(4)	0.3341(2)	0.036(1)
C(7)	0.5186(4)	0.1057(4)	0.3595(2)	0.031(1)
N(8)	0.4325(4)	0.0495(3)	0.2991(2)	0.0342(9)
C(9)	0.3603(5)	-0.0542(4)	0.3139(3)	0.038(1)
C(10)	0.2204(4)	-0.0368(3)	0.3402(2)	0.032(1)
N(11)	0.2423(3)	0.0015(3)	0.4289(2)	0.0295(8)
C(12)	0.1483(4)	0.0975(3)	0.4415(2)	0.032(1)
C(13)	0.2002(4)	0.2048(3)	0.4079(2)	0.031(1)
C(14)	0.0992(4)	0.3008(3)	0.4138(2)	0.032(1)
O(5)	0.6001(3)	0.3318(3)	0.4512(2)	0.0454(9)
O(7)	0.5387(3)	0.0770(3)	0.4325(2)	0.0429(8)
O(W)	0.1587(4)	-0.1983(2)	0.4918(2)	0.0469(9)
H(11)	0.144(6)	0.398(5)	0.321(3)	0.05*
H(12)	0.066(6)	0.459(5)	0.374(3)	0.05*
H(4)	0.398(6)	0.358(5)	0.287(3)	0.05*
H(8)	0.409(6)	0.077(5)	0.253(3)	0.05*
H(111)	0.213(6)	-0.060(5)	0.454(3)	0.05*
H(112)	0.333(6)	0.015(5)	0.445(3)	0.05*
H(W1)	0.120(6)	-0.228(5)	0.457(3)	0.05*
H(W2)	0.220(6)	-0.224(4)	0.488(3)	0.05*

\*Isotropically refined selected hydrogen atoms participating in H-bonding.

Table II. Interatomic distances (Å), angles (deg.) and torsional angles (deg.)

I. $PtCl_4^{2-}$ anion			
Pt—Cl(1)	2.297(1)	Pt—Cl(3)	2.316(1)
Pt—Cl(2)	2.309(2)	Pt—Cl(4)	2.302(2)
Cl(1)—Pt—Cl(2)	89.10(4)	Cl(2)—Pt—Cl(3)	91.52(4)
Cl(1)—Pt—Cl(3)	176.73(4)	Cl(2)—Pt—Cl(4)	176.35(4)
Cl(1)—Pt—Cl(4)	89.26(4)	Cl(3)—Pt—Cl(4)	90.30(5)
II. Diprotonated Dioxocyclam Ligand			
N(1)—C(2)	1.511(6)	C(7)—N(8)	1.328(5)
N(1)—C(14)	1.503(5)	C(7)—O(7)	1.234(5)
C(2)—C(3)	1.517(7)	N(8)—C(9)	1.462(6)
C(3)—N(4)	1.455(6)	C(9)—C(10)	1.505(6)
N(4)—C(5)	1.342(5)	C(10)—N(11)	1.512(6)
C(5)—C(6)	1.519(7)	N(11)—C(12)	1.496(5)
C(5)—O(5)	1.226(5)	C(12)—C(13)	1.522(6)
C(6)—C(7)	1.518(7)	C(13)—C(14)	1.513(6)
C(2)—N(1)—C(14)	115.1(3)	C(6)—C(7)—O(7)	121.5(3)
N(1)—C(2)—C(3)	111.7(3)	N(8)—C(7)—O(7)	122.5(4)
C(2)—C(3)—N(4)	114.0(4)	C(7)—N(8)—C(9)	122.4(3)
C(3)—N(4)—C(5)	122.0(3)	N(8)—C(9)—C(10)	114.3(3)
N(4)—C(5)—C(6)	116.1(3)	C(9)—C(10)—N(11)	112.7(4)
N(4)—C(5)—O(5)	122.1(4)	C(10)—N(11)—C(12)	114.3(3)
C(6)—C(5)—O(5)	122.0(3)	N(11)—C(12)—C(13)	109.8(3)
C(5)—C(6)—C(7)	109.8(4)	C(12)—C(13)—C(14)	110.5(4)
C(6)—C(7)—N(8)	116.1(3)	N(1)—C(14)—C(13)	111.0(3)
C(14)—N(1)—C(2)—C(3)	128.2(4)	C(6)—C(7)—N(8)—C(9)	179.1(4)
N(1)—C(2)—C(3)—N(4)	-65.3(4)	O(7)—C(7)—N(8)—C(9)	-3.2(6)
C(2)—C(3)—N(4)—C(5)	-79.9(5)	C(7)—N(8)—C(9)—C(10)	84.6(5)
C(3)—N(4)—C(5)—C(6)	-178.1(4)	N(8)—C(9)—C(10)—N(11)	-75.0(4)
C(3)—N(4)—C(5)—O(5)	3.4(6)	C(9)—C(10)—N(11)—C(12)	133.9(3)
N(4)—C(5)—C(6)—C(7)	-100.9(4)	C(10)—N(11)—C(12)—C(13)	-72.4(4)
O(5)—C(5)—C(6)—C(7)	77.5(5)	N(11)—C(12)—C(13)—C(14)	175.4(3)
C(5)—C(6)—C(7)—N(8)	120.8(4)	C(12)—C(13)—C(14)—N(1)	-177.5(3)
C(5)—C(6)—C(7)—O(7)	-57.0(5)	C(13)—C(14)—N(1)—C(2)	-67.8(4)

The crystal structure consists of diprotonated dioxocyclam, discrete  $PtCl_4^{2-}$  anions and water molecules linked together by an extensive network of hydrogen bonds. Cations and anions are stacked in alternating order in columns running down the  $c$  axis; the water molecules filling up the intercolumnar space (Figure 2). The  $PtCl_4^{2-}$  anion, situated in general positions, has a square planar configuration slightly distorted towards the tetrahedron. Chlorine atoms [in the sequence Cl(1)—Cl(4)] deviated from the best-fit plane through the anion by  $-0.10$ ,  $0.09$ ,  $-0.03$ , and  $0.04$  Å, respectively; Pt lies exactly in the plane. Pt—Cl bond lengths vary within  $0.019$  Å; however, the two averages of *trans*-disposed Pt—Cl distances are the same:  $2.306$  Å.

Table III. Geometry of the hydrogen bonds

D—H...A, A'	D—H (Å)	H...A (Å)	D...A (Å)	D—H...A (deg.)	A...H...A' (deg.)
N(1)—H(11)...Cl(2)	0.93(5)	2.31(5)	3.238(4)	176(5)	
N(1)—H(12)...Cl(3) <sup>i</sup>	0.98(6)	2.82(6)	3.4513(4)	123(4)	79(2)
...Cl(4) <sup>i</sup>		2.27(6)	3.193(4)	157(5)	
N(4)—H(4)...Cl(2)		2.65(5)	3.321(3)	138(5)	
N(8)—H(8)...Cl(1)	0.81(5)	2.82(5)	3.600(4)	163(5)	68(1)
...Cl(4)		2.97(5)	3.521(3)	128(5)	
N(11)—H(111)...O(W)	0.92(6)	1.88(6)	2.788(4)	172(5)	
N(11)—H(112)...O(7)	0.86(5)	2.14(6)	2.948(5)	155(5)	86(2)
...O(7) <sup>ii</sup>		2.39(5)	2.896(4)	118(5)	
O(W)—H(W1)...Cl(3) <sup>iii</sup>	0.71(5)	2.77(5)	3.445(3)	159(5)	
O(W)—H(W2)...O(5) <sup>ii</sup>	0.67(6)	2.20(5)	2.780(4)	146(6)	

D and A denote H-bond donor and acceptor, respectively.

Symmetry codes: (i)  $-x, 1/2 + y, 1/2 - z$

(ii)  $1 - x, -y, 1 - z$

(iii)  $-x, -1/2 + y, 1/2 - z$

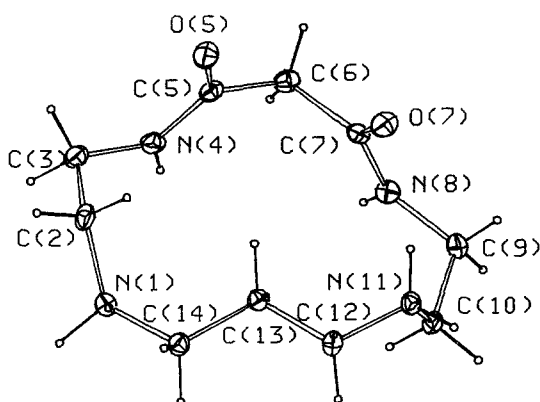


Fig. 1. A view of the diprotonated dioxocyclam molecule and the atom numbering scheme. 30% thermal ellipsoids, H atoms are shown as small spheres of arbitrary radii.

The macrocycle conformation is governed by three factors: the nature of the ring itself, containing two planar peptide fragments bridged via a methylene group; the arrangement of the planar  $\text{PtCl}_4^{2-}$  groups in columns; and the extensive hydrogen bonding network. The seven-atom ring subunit  $\text{CH}_2(-\text{CO}-\text{NH}-\text{CH}_2-)_2$ , containing two peptide moieties, exhibits a  $C_s$  pseudosymmetry and has an 'open' chair conformation. The sequence of torsional angles over the chain  $\text{C}(2)-\text{C}(3)-\text{N}(4)-\text{C}(5)-\text{C}(6)-\text{C}(7)-\text{N}(8)-\text{C}(9)-\text{C}(10)$  is  $(-sc, ap, -ac, ac, ap, +sc)$  {ideal values are:  $sc-(\pm 60)$ ,  $ac(\pm 120)$ ,  $ap(180^\circ)$  [11]}. The peptide moieties  $-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2-$  exhibit a high degree of planarity; the torsion angles are  $-178.1(4)^\circ$  and  $179.1(4)^\circ$ ,

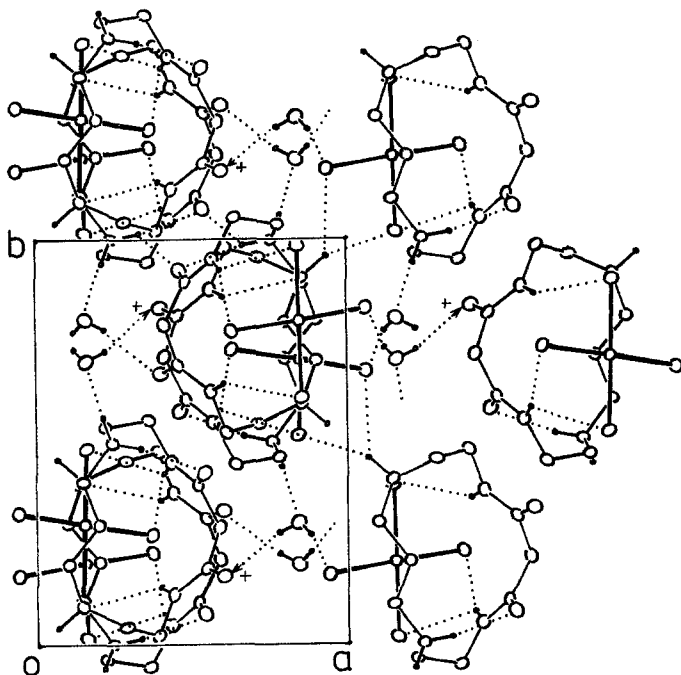


Fig. 2. Columnar arrangement of the diprotonated macrocycle and its  $\text{PtCl}_4^{2-}$  counterion. Channels between the columns are filled by water molecules.

for sequences involving N(4) and N(8), respectively. Both O and amido H atoms have an axial orientation in the half-ring.

The conformation of the rest of the macrocycle is predetermined by the presence of  $\text{PtCl}_4^{2-}$  anions arranged in columns. A part of the macrocycle is sandwiched by these planar anions thus adopting a flattened shape (Figure 3) with an *endo*-orientation with respect to the central cavity atom C(13). The torsion angles in the flat five-atom segment N(11)–C(12)–C(13)–C(14)–N(1) are  $175.4(3)^\circ$  and  $-177.5(3)^\circ$ . The full sequence of idealized torsion angles in the second molecular subunit is  $(-sc, ac, -sc, ap)_2$  and proves its  $C_2$  pseudosymmetry shape. No unusual bond distances and angles are encountered in the macrocycle.

The dioxocyclam ligand has been designed as a chelating agent capable of accommodating platinum(II) [2]. The structure of  $[\text{Pt}(\text{H}_2\text{L}') \cdot 5 \text{H}_2\text{O}]$ ,  $\text{L}' = 6$ -methylidioxocyclam [3], shows Pt in a square planar cavity of four N atoms. An intermediate complexation takes place in  $[\text{PtLCl}_2] \cdot 2 \text{H}_2\text{O}$ , [3], where Pt forms only two coordinate bonds with the ligand. In both cases the two nonpeptide N atoms are turned to the amino-state and point to the centre of the cavity, taking part in coordination to Pt. In the present structure the same nitrogens are deprotonated forming the amino  $-\text{NH}_2$  groups. However, one of them, N(1), is in an *exo*-orientation with respect to the ring. As a result the N(11)⋯N(1) distance of  $4.951(5) \text{ \AA}$  between two amino N atoms in the flattened part of the macrocycle is much greater

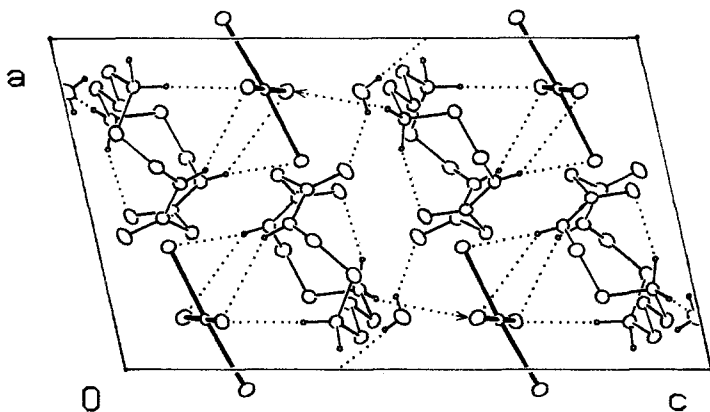


Fig. 3. Projection of the structure down the  $b$  axis. The macrocycle 'open' chair part and the flattened segment are clearly seen. H-bonds are indicated by dashed lines.

than the three other distances,  $N(1)\cdots N(4)$  3.049(5),  $N(4)\cdots N(8)$  3.941(5), and  $N(8)\cdots N(11)$  3.161(5) Å.

The two peptide  $H-N-C=O$  fragments of the macrocycle participate in an intermolecular hydrogen bonding both as donors (of the type  $N-H\cdots Cl$ ) and acceptors [ $O(5)\cdots H-O(W)$ ;  $O(7)\cdots H-N$ ]. The amino groups form H-bonds with chlorine [ $N(1)$  with  $Cl(2)$ ,  $Cl(3)$ ,  $Cl(4)$ ] or oxygen [ $N(11)$  with  $O(W)$ ,  $O(7)$ ]. The water molecule contributes twice to the H-bonding network by its H atoms [ $O(W)-H(W1)\cdots Cl(3)$ ,  $O(W)-H(W2)\cdots O(5)$ ], plays an acceptor role in the  $O(W)\cdots H(111)-N(11)$  linking, and weakly interacts with a favourably situated methylene hydrogen  $H(142)$  [ $O\cdots H$  2.93(6),  $H-C$  1.01(6) Å,  $O\cdots H-C$  110(4)°,  $O\cdots C$  3.420(6) Å].

The magnetic properties of the ionic complex salt was studied by the EPR method in the temperature range 100–330 K. The polycrystalline sample showed weak temperature dependent paramagnetism (Figure 4). At high temperature (330 K) more than three EPR signals are observed. The first at about 3500 G has a temperature dependent  $g$ -value. Its intensity decreases with temperature and disappears at 170 K. In the 3000–3500 G range there is a group of signals, again with temperature dependent linewidths. They exhibit a maximum intensity at 140 K. A low-field EPR signal is observed at lower temperatures (below 170 K).

As can be seen from Figures 1–3 the complex exhibits integrated ionic stacking [13] from alternating planar transition metal complex ions ( $PtCl_4^{2-}$ ) and the flattened part of the flexible protonated dioxocyclam molecule involving both peptide  $H-N-C=O$  fragments. It seems likely that the paramagnetism observed is due to localized bonds at a structural defect or a significant charge-transfer interaction between the  $\pi$ -systems of the peptide fragments and the  $d_z$  antibonding orbitals of Pt(II) along the stack ( $c$ ) axes. From this point of view the orientation dependence of the EPR spectrum observed in the polycrystalline sample might be expected.

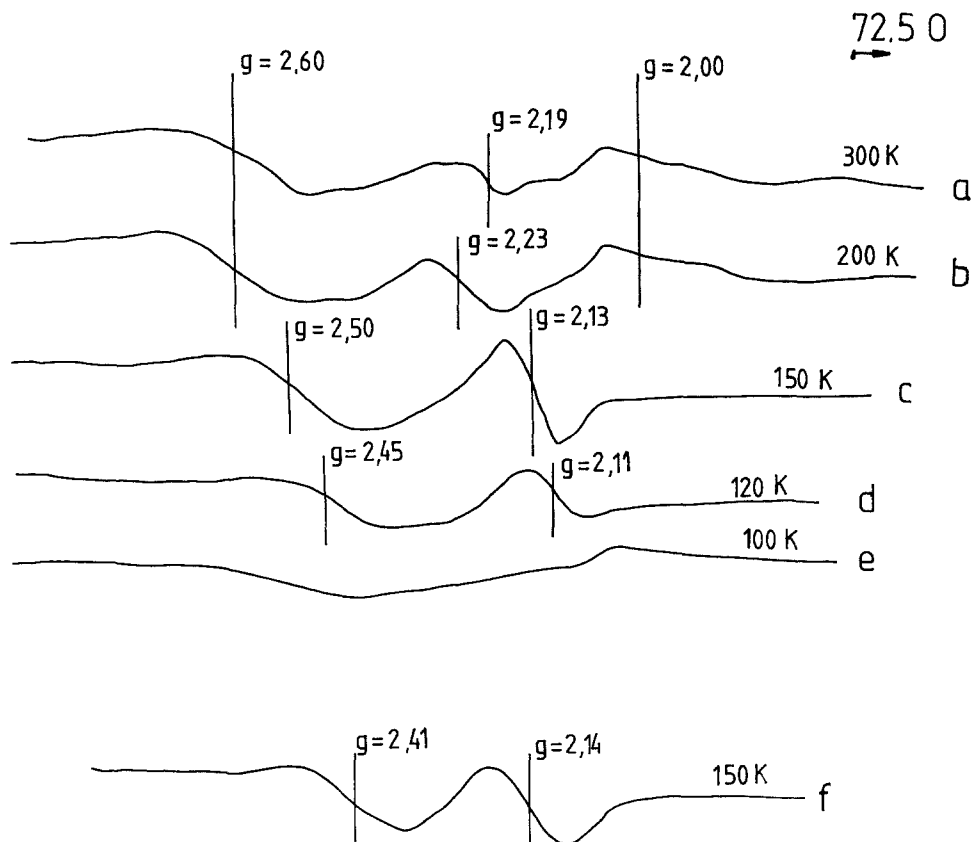


Fig. 4. Temperature and orientation dependences of the EPR spectrum of a polycrystalline sample of the integrated ionic stack complex salt: (a-e) EPR spectra of a polycrystalline sample with the same arbitrary orientation at different temperatures; (f) EPR spectrum of the sample at another orientation at 150 K.

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